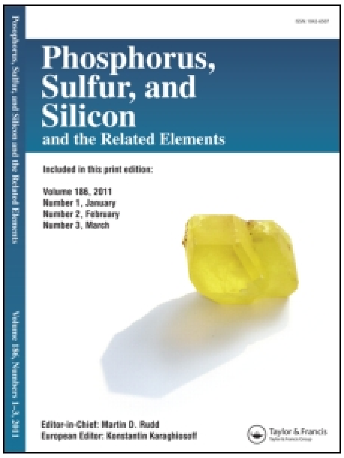


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF DIMETHYL HALOSULFONIUM SALTS (II)[1] The Reaction of $(CH_3)_2SBr_2$ with Carbanions and Amide Anions

Naomichi Furukawa[a]; Teruhiko Inoue[a]; Tetsuo Aida[a]; Takeshi Akasaka[a]; Shigeru Oae[a]
[a] Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki, Japan

To cite this Article Furukawa, Naomichi , Inoue, Teruhiko , Aida, Tetsuo , Akasaka, Takeshi and Oae, Shigeru(1978) 'THE REACTION OF DIMETHYL HALOSULFONIUM SALTS (II)[1] The Reaction of $(CH_3)_2SBr_2$ with Carbanions and Amide Anions', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 1, 15 — 17

To link to this Article: DOI: 10.1080/03086647808079957

URL: http://dx.doi.org/10.1080/03086647808079957

Phosphorus and Sulfur
1978, Vol. 4 pp. 15–17

THE REACTION OF DIMETHYL HALOSULFONIUM SALTS (II)[1]

The Reaction of $(CH_3)_2SBr_2$ with Carbanions and Amide Anions

NAOMICHI FURUKAWA, TERUHIKO INOUE,[2] TETSUO AIDA, TAKESHI AKASAKA
and SHIGERU OAE

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

(*Received April 28, 1977*)

Some active methylene compounds such as diethylmalonate were dimerized by treating with dimethyl bromosulfonium bromide (DMBS) or diphenyl bromosulfonium bromide (DPBS) in the presence of a strong base. The reaction of DMBS with sodium *p*-tolylsulfonamide afforded dimethyl N-*p*-tosylsulfilimine quantitatively.

DMBS is readily prepared from dimethyl sulfide and bromine and is a stable crystalline compound.[3] Recently, we found that DMBS can convert various alcohols to the corresponding alkyl bromides in good yields.[4] Since the reaction is highly stereospecific and has high selectivities toward alcohols, DMBS and the related halosulfonium salts are considered to be rather unique synthetic reagents. Thus, in order to expand further utilization of DMBS, we have treated it with nucleophiles such as carbanions or sulfonamide anions with the hope of opening new paths to S-ylides, sulfonium salts or sulfilimines.

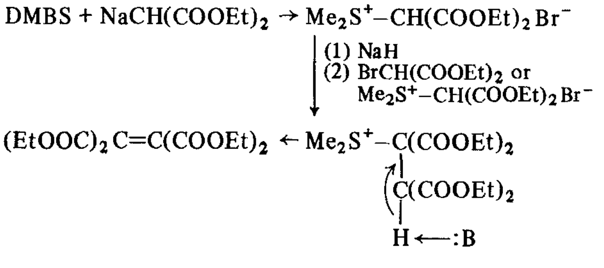
In this paper we describe a new representative reaction of DMBS (DPBS) with active methylene compounds and sulfonamide anion in the presence of a strong base.

RESULTS AND DISCUSSION

The Reaction with Active Methylene Compounds

The reaction was carried out by adding an aliquot of DMBS in methylene chloride to a methylene chloride solution of 1 mol equivalent of an active methylene compound and 2 mol equivalent of sodium hydride at a temperature ranging from –5 to –10°C. After stirring the solution at room temperature for 2 hr, the products were separated by column chromatography and identified by means of spectroscopic and GLC analyses. The products obtained by the reaction are summarized in Table I.

The results summarized in Table I show that the major products obtained are not S-ylides as we expected but either the olefins derived from the dimerization of the active methylene compounds or the α-brominated ketones or both. Harris reported that dicyanobromomethane was found to dimerize similarly to tetracyanoethylene in the presence of diphenyl sulfide.[5] In the case of diethylmalonate, when the reaction was carried out with DMBS or DPBS, a careful product analysis has shown that methyl diethyl malonyl sulfide or S,S-diphenyl dicarboethoxy S-ylide was detected. These observations seem to suggest that the sulfur atom of DMBS (DPBS) serves as the reaction center for the dimerization of the active methylene compounds. Therefore, it may be concluded that the reaction may proceed via the initial formation of a sulfonium salt, generated from bromodiethylmalonate and dimethyl sulfide, which in the subsequent step forms S-ylide that undergoes nucleophilic attack on brominated malonate or the sulfonium salt affording a corresponding sulfonium salt; final elimination of the sulfide affords the olefin, as shown below.[6]

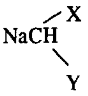
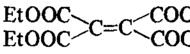
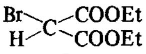
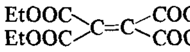
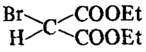
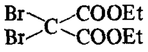
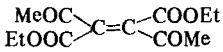
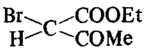
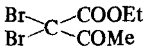
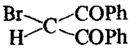
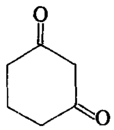
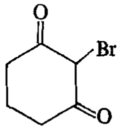
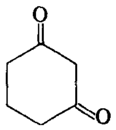


$$\begin{tikzcd} \mathrm{DMBS} + \mathrm{NaCH(COOEt)_2} \arrow[r] & \mathrm{Me_2S^+{-}CH(COOEt)_2\,Br^-} \arrow[d, "\begin{array}{l}(1)\ \mathrm{NaH}\\ (2)\ \mathrm{BrCH(COOEt)_2}\ \text{or}\\ \quad \mathrm{Me_2S^+{-}CH(COOEt)_2Br^-}\end{array}"] \\ \mathrm{(EtOOC)_2C{=}C(COOEt)_2} & \begin{array}{l}\mathrm{Me_2S^+{-}C(COOEt)_2}\\ \qquad | \\ \qquad \mathrm{C(COOEt)_2}\\ \qquad | \\ \qquad \mathrm{H \leftarrow :B}\end{array} \arrow[l] \end{tikzcd}$$

The formation of dimethyl diethylmalonylsulfonium bromide was accompanied by the reaction of bromodiethylmalonate, formed by the attack of the carbanion on the bromine atom of DMBS, with the sulfide that is originated from DMBS. Evidence supporting this argu-

TABLE I

The reaction of active methylene compounds with DMBS

 X	Y	Products and yields (%)		
–COOEt	–COOEt	 (56.5)	 (5.7)	
–COOEt	–COOEt[a]	 (36.7)	 (47.6)	 (3.7)
–COMe	–COOEt	 (33.5)	 (10.0)	 (1.3)
–COPh	–COPh	 (89.2)	PhCOCH$_2$COPh recovered	
		 (57.5)	 recovered	

[a] The reaction was carried out with DPBS.

ment is that all active methylene compounds afforded the corresponding mono-brominated compounds and that when a Grignard reagent, made from iodobenzene and magnesium, reacted with DMBS, bromobenzene is formed in an almost quantitative yield.

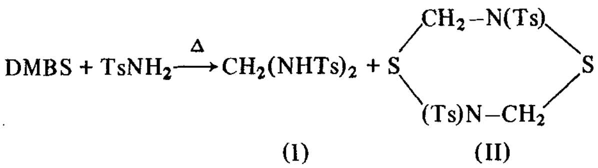
The Reaction with Sulfonamide

A methylene chloride solution of *p*-toluenesulfonamide (TsNH$_2$) and sodium hydride was added to a methylene chloride solution of one molar equivalent of DMBS (DPBS) at room temperature and stirring continued for 10 hr. After general work up, dimethyl N-*p*-tosylsulfilimine[7] (diphenyl N-*p*-tosylsulfilimine) was afforded quantitatively.

The reaction should proceed via a similar mechanistic route as mentioned for the formation of the S-ylide in the reaction of active methylene compounds. Bromo *p*-toluenesulfonamide was initially formed and reacted with dimethyl sulfide in analogy with the reaction of sulfide with sodium N-chloro-*p*-toluenesulfonamide (Chloramine-T) affording the corresponding N-*p*-tosylsulfilimine.[7]

$$\text{DMBS} + \text{TsNH}_2 \xrightarrow{\text{NaH}} [\text{TsNHBr}] \xrightarrow{\text{MeSMe}} \begin{array}{c}\text{MeSMe}\\ \downarrow\\ \text{NTs}\end{array}$$

The reaction did not proceed at all in the absence of sodium hydride at room temperature. However, when a carbon tetrachloride solution of DMBS and TsNH$_2$ was refluxed for 8 hr, two compounds (I), (II) were isolated in 10% and 20% yields, respectively.



(I) (II)

Since the products (I) and (II) are known to be the pyrolysis products of dimethyl N-*p*-tosylsulfilimine,[8] the reaction is considered to proceed via the intermediate formation of the corresponding sulfilimine.

Consequently, DMBS (DPBS) acts as an oxidizing reagent in the dimerization of active methylene compounds and a precursor for the corresponding N-*p*-tosylsulfilimine.

EXPERIMENTAL

The Reaction of DMBS (DPBS) with Active Methylene Compounds

A typical run was as follows. 10 ml of a well-cooled methylene chloride solution of DMBS (4.5 mmol) was added to a methylene chloride solution of diethylmalonate (4.5 mmol) and a twofold excess of sodium hydride (10 mmol) at a temperature ranging from –5 to –10°C. After stirring the solution at room temperature for 2 hr, the reaction mixture was poured into ice-water. The organic layer was separated and dried over anhydrous sodium sulfate. After evaporating the solvent, the products obtained were separated by column chromatography with silica gel using benzene as an eluent, and identified by means of spectroscopic and GLC analyses. Tetracarboethoxyethylene and bromodiethylmalonate were obtained in 56.5% and 5.7% yields, respectively. The results obtained are summarized in Table I.

The Reaction of DMBS (DPBS) with $TsNH_2$ in the Presence of Sodium Hydride

A methylene chloride solution of DMBS (4.6 mmol) was added to a methylene chloride solution of $TsNH_2$ (4.6 mmol) and sodium hydride (10 mmol) at room temperature. After stirring the solution for 10 hr, the reaction mixture was poured into ice-water and the organic layer was washed with 5% aqueous sodium hydroxide solution to exclude unreacted $TsNH_2$ and dried over anhydrous sodium sulfate. After evaporating the solvent, only dimethyl N-*p*-tosylsulfilimine was obtained in quantitative yield.

The reaction of DMBS (4.6 mmol) with $TsNH_2$ (4.6 mmol) in 30 ml of carbon tetrachloride was carried out by refluxing for 8 hr. After the reaction, the solvent was evaporated and the reaction mixture obtained was extracted with chloroform and washed with 5% aqueous sodium hydroxide solution. The solvent was evaporated and solidified products obtained dissolved in ethanol by heating. After cooling, (II) was isolated by filtration in 20% yield, mp., 158.5–160°C. When chloroform was added to the filtrate, (I) (10% yield) was deposited and identified by spectroscopic comparison with an authentic sample prepared by the reaction of formaldehyde with $TsNH_2$ in aqueous sodium hydroxide solution.

REFERENCES AND NOTES

1. Part 1, N. Furukawa, T. Inoue, T. Aida and S. Oae, *Chem. Commun.* **1973**, 213.
2. Present address; Ube Ind. Ltd., Ube, Yamaguchi 755 Japan.
3. C. F. Bobery, G. Winter and G. R. Schultz, *Chem. Ber.* **89**, 1160 (1965); H. Bohme and E. Boll, *Z. Anorg. Allg. Chem.* **290**, 17 (1957).
4. N. Furukawa, T. Inoue, T. Aida and S. Oae, *Chem. Commun.* **1973**, 213; E. J. Corey, C. H. Kim and M. Takeda, *Tetrahedron Lett.* **1973**, 4339.
5. J. E. Harris, U.S. Patent 3, 300, 853 (1967).
6. H. Nozaki, K. Kondo and M. Takaya, *Tetrahedron Lett.* **1965**, 251; A. W. Johnson and R. T. Amel, *Tetrahedron Lett.* **1966**, 819.
7. K. Tsujihara, N. Furukawa, K. Oae and S. Oae, *Bull. Chem. Soc. Japan* **42**, 2631 (1969).
8. S. Oae, T. Aida, K. Tsujihara and N. Furukawa, unpublished results.